



(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **94810345.2**

(51) Int. Cl.⁵: **C11D 3/34, C11D 3/26**

(22) Date of filing: **10.06.94**

(30) Priority: **19.06.93 GB 9312693**
08.12.93 GB 9325117

(43) Date of publication of application:
28.12.94 Bulletin 94/52

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI NL PT SE

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(54) **Inhibition of re-absorption of migrating dyes in the wash liquor.**

(57) A process for inhibiting the re-absorption of migrating dyes in the wash liquor comprises introducing into a wash liquor containing a peroxide-containing detergent, from 0.5 to 150 mg, per litre of wash liquor, of one or more manganese compounds having the formula (1), (2), (3), (4), (5), (6) or (7) as defined in the specification. The manganese compounds do not exhaust at all on to cotton, polyamide or polyester fibres so that the compounds cannot lead to fibre discolouration problems.

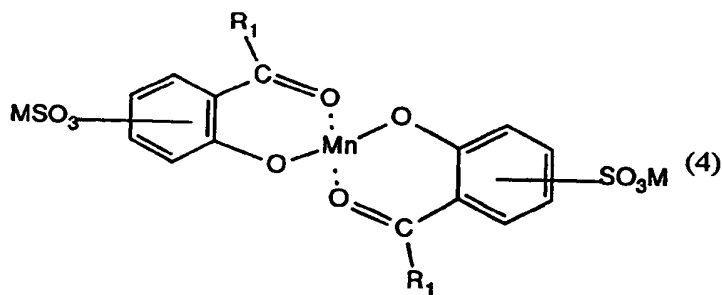
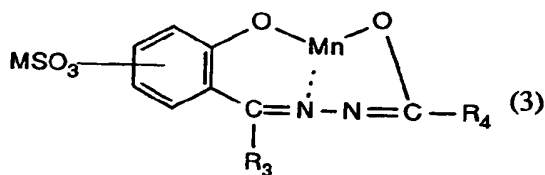
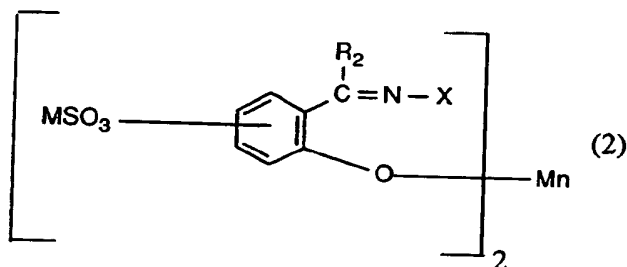
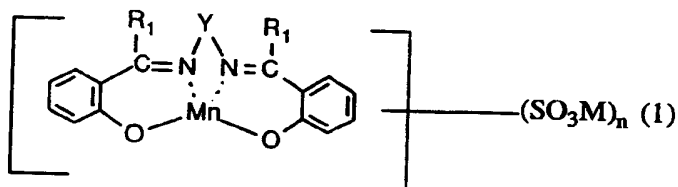
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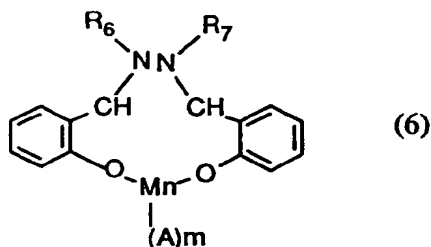
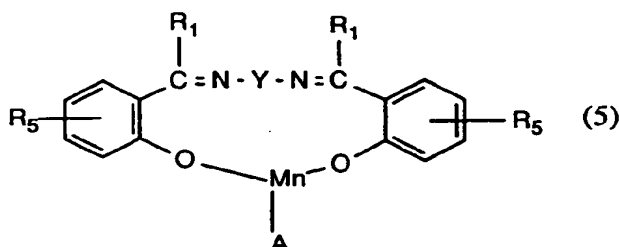
The present invention relates to a process for inhibiting the re-absorption of migrating dyes in the wash liquor.

It is well known that various metal compounds, e.g. manganese complexes, are useful in detergents as catalysts for peroxides.

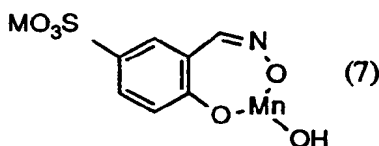
It has now been found that certain other manganese complexes, although effecting no apparent improvement in the bleaching power of peroxides, exert a pronounced bleaching effect on dirt or dyes in the wash bath. Moreover, these manganese complexes do not exhaust at all on cotton, polyamide or polyester fibres so that the complexes cannot lead to fibre discolouration problems.

Accordingly, the present invention provides a process for inhibiting the re-absorption of migrating dyes in the wash liquor, comprising introducing into a wash liquor containing a peroxide-containing detergent, from 0.5 to 150, preferably from 1.5 to 75, especially from 7.5 to 40 mg, per litre of wash liquor, of one or more compounds having the formula (1), (2), (3), (4), (5), (6) or (7):

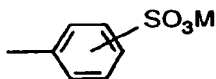




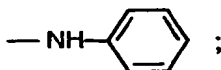
or



in which R_1 , R_2 , R_3 and R_4 are the same or different and each is hydrogen or optionally substituted alkyl, cycloalkyl or aryl; R_5 is hydrogen, alkyl or SO_3M ; R_6 and R_7 are the same or different and each is NH-CO-NH_2 , a group of formula



or a group of formula



Y is optionally substituted alkylene or cyclohexylene; X is OH , NH_2 , optionally substituted aryl or optionally substituted alkyl; n is 0, 1, 2 or 3; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine; m is 0 or 1; and A is an anion.

When one or more of R_1 , R_2 , R_3 , R_4 , R_5 and X are optionally substituted alkyl, preferred alkyl groups are $\text{C}_1\text{-C}_8$, especially $\text{C}_1\text{-C}_4$ -alkyl groups. The alkyl groups may be branched or unbranched and may be optionally substituted, e.g. by halogen such as fluorine, chlorine or bromine, by $\text{C}_1\text{-C}_4$ -alkoxy such as methoxy or ethoxy, by phenyl or carboxyl, by $\text{C}_1\text{-C}_4$ -alkoxycarbonyl such as acetyl, or by a mono- or di-alkylated amino group.

When one or more of R_1 , R_2 , R_3 , R_4 and R_5 are cycloalkyl, this may also be substituted, e.g. by $\text{C}_1\text{-C}_4$ -alkyl or $\text{C}_1\text{-C}_4$ -alkoxy.

When one or more of R_1 , R_2 , R_3 , R_4 , R_5 and X are optionally substituted aryl, they are preferably a phenyl or naphthyl group which may be substituted by $\text{C}_1\text{-C}_4$ -alkyl, e.g. by methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec.-butyl or tert.-butyl, by $\text{C}_1\text{-C}_4$ -alkoxy such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec.-butoxy or tert.-butoxy, by halogen such as fluorine, chlorine or bromine, by $\text{C}_2\text{-C}_5$ -alkanoylamino,

such as acetyl amino, propionyl amino or butyryl amino, by nitro, sulpho or by dialkylated amino.

When Y is alkylene, it is preferably a C₂-C₄-alkylene residue, especially a -CH₂-CH₂-bridge. Y may also be a C₂-C₈-alkylene residue which is interrupted by oxygen or, especially, by nitrogen, in particular the -(CH₂)₃-NH-(CH₂)₃- bridge.

5 Anions A include halide, especially chloride, sulphate, nitrate, hydroxy, methoxy, BF₄, PF₆, carboxylate, especially acetate, triflate or tosylate.

With respect to the compounds of formula (1), preferably each R₁ is hydrogen, Y is the ethylene bridge and n is 2, whereby one sulpho group is preferably present in each benzene ring, especially in para position to the oxygen atom.

10 In relation to the compounds of formula (2), preferably R₂ is hydrogen and X is OH.

With respect to the compounds of formula (3), preferred compounds are those in which R₃ is hydrogen and R₄ is hydrogen, methyl or, especially, phenyl. Especially preferred compounds are those in which the SO₃M group is in para position to the oxygen atom.

With respect to the compounds of formula (4), preferred compounds are those in which R₁ is hydrogen, more especially those in which each SO₃M group is in para position to the respective oxygen atom.

15 As to the compounds of formula (5), preferably R₁ is hydrogen or methyl, R₅ is hydrogen, methyl or SO₃Na and is preferably in p-position with respect to the oxygen atom, Y is -CH₂CH₂- or cyclohexylene and A is a chloride, acetate, hydroxy, methoxy or PF₆ anion.

20 In relation to the compounds of formula (6), preferably R₆ and R₇ are the same. The preferred anion, when present, is acetate.

In each of the compounds of formula (1) to (7), it is preferred that they are used in neutral form, i.e. that M, when present, is other than hydrogen, preferably a cation formed from an alkali metal, in particular sodium, or from an amine.

25 Moreover, in each of the compounds of formula (1) to (7), the respective benzene rings may contain, in addition to any sulpho group, one or more further substituents such as C₁-C₄-alkyl, C₁-C₄-alkoxy, halogen, cyano or nitro.

The manganese complexes of formula (2) to (7) are believed to be new compounds and, as such, form a further aspect of the present invention. They may be produced by known methods, e.g. by the methods analogous to those disclosed in US Patent 4,655,785 relating to similar copper complexes.

30 The present invention also provides a detergent composition comprising:

- i) 5-90%, preferably 5-70% of A) an anionic surfactant and/or B) a nonionic surfactant;
- ii) 5-70%, preferably 5-50%, especially 5-40% of C) a builder;
- iii) 0.1-30%, preferably 1-12% of D) a peroxide; and

35 iv) 0.005-2%, preferably 0.02-1%, especially 0.1-0.5% of E) a compound of formula (1) to (7) as defined above, each by weight, based on the total weight of the detergent.

The detergent may be formulated as a solid; or as a non-aqueous liquid detergent, containing not more than 5, preferably 0-1 wt.% of water, and based on a suspension of a builder in a non-ionic surfactant, as described, e.g., in GB-A-2158454.

40 Preferably, the detergent is in powder or granulate form.

Such powder or granulate forms may be produced by firstly forming a base powder by spray-drying an aqueous slurry containing all the said components, apart from the components D) and E); then adding the components D) and E) by dry-blending them into the base powder. In a further process, the component E) may be added to an aqueous slurry containing components A), B) and C), followed by spray-drying the slurry prior to dry-blending component D) into the mixture. In a still further process, component B) is not present, or is only partly present in an aqueous slurry containing components A) and C); component E) is incorporated into component B), which is then added to the spray-dried base powder; and finally component D) is dry-blended into the mixture.

The anionic surfactant component A) may be, e.g., a sulphate, sulphonate or carboxylate surfactant, or a mixture of these.

50 Preferred sulphates are alkyl sulphates having 12-22 carbon atoms in the alkyl radical, optionally in combination with alkyl ethoxy sulphates having 10-20 carbon atoms in the alkyl radical.

Preferred sulphonates include alkyl benzene sulphonates having 9-15 carbon atoms in the alkyl radical.

In each case, the cation is preferably an alkali metal, especially sodium.

55 Preferred carboxylates are alkali metal sarcosinates of formula R-CO(R¹)CH₂COOM¹ in which R is alkyl or alkenyl having 9-17 carbon atoms in the alkyl or alkenyl radical, R¹ is C₁-C₄ alkyl and M¹ is alkali metal.

The nonionic surfactant component B) may be, e.g., a condensate of ethylene oxide with a C₉-C₁₅ primary alcohol having 3-8 moles of ethylene oxide per mole.

The builder component C) may be an alkali metal phosphate, especially a tripolyphosphate; a carbonate

or bicarbonate, especially the sodium salts thereof; a silicate; an aluminosilicate; a polycarboxylate; a polycarboxylic acid; an organic phosphonate; or an aminoalkylene poly (alkylene phosphonate); or a mixture of these.

Preferred silicates are crystalline layered sodium silicates of the formula $\text{NaHSi}_m\text{O}_{2m+1}\cdot p\text{H}_2\text{O}$ or $\text{Na}_2\text{Si}_m\text{O}_{2m+1}\cdot p\text{H}_2\text{O}$ in which m is a number from 1.9 to 4 and p is 0 to 20.

Preferred aluminosilicates are the commercially-available synthetic materials designated as Zeolites A, B, X, and HS, or mixtures of these. Zeolite A is preferred.

Preferred polycarboxylates include hydroxypolycarboxylates, in particular citrates, polyacrylates and their copolymers with maleic anhydride.

Preferred polycarboxylic acids include nitrilotriacetic acid and ethylene diamine tetra-acetic acid.

Preferred organic phosphonates or aminoalkylene poly (alkylene phosphonates) are alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates.

The peroxide component D) may be any organic or inorganic peroxide compound, described in the literature or available on the market, which bleaches textiles at conventional washing temperatures, e.g. temperatures in the range of from 10°C. to 90°C. In particular, the organic peroxides are, for example, monoperoxides or polyperoxides having alkyl chains of at least 3, preferably 6 to 20, carbon atoms; in particular diperoxydicarboxylates having 6 to 12 C atoms, such as diperoxyperazates, diperoxypersebates, diperoxyphthalates and/or diperoxydodecanedioates, especially their corresponding free acids, are of interest. It is preferred, however, to employ very active inorganic peroxides, such as persulphate, perborate and/or percarbonate. It is, of course, also possible to employ mixtures of organic and/or inorganic peroxides.

The addition of the peroxides to the detergent is effected, in particular, by mixing the components, for example by means of screw-metering systems and/or fluidized bed mixers.

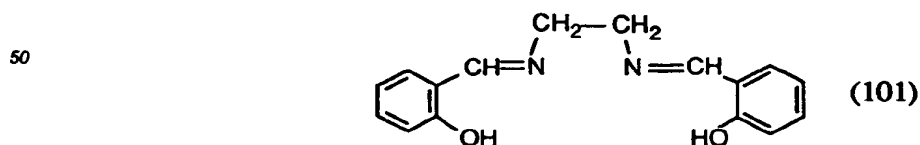
The detergents may contain, in addition to the combination according to the invention, one or more of fluorescent whitening agents, such as a bis-triazinylamino-stilbene-disulphonic acid, a bis-triazolyl-stilbene-disulphonic acid, a bis-styryl-biphenyl, a bis-benzofuranyl-biphenyl, a bis-benzoxalyl derivative, a bis-benzimidazolyl derivative, a coumarine derivative or a pyrazoline derivative; soil suspending agents, for example sodium carboxymethylcellulose; salts for adjusting the pH, for example alkali or alkaline earth metal silicates; foam regulators, for example soap; salts for adjusting the spray drying and granulating properties, for example sodium sulphate; perfumes; and also, if appropriate, antistatic and softening agents; such as smectite clays; enzymes, such as amylases; photobleaching agents; pigments; and/or shading agents. These constituents should, of course, be stable to the bleaching system employed.

A particularly preferred detergent co-additive is a polymer known to be useful in preventing the transfer of labile dyes between fabrics during the washing cycle. Preferred examples of such polymers are polyvinyl pyrrolidones, optionally modified by the inclusion of an anionic or cationic substituent, especially those having a molecular weight in the range from 5000 to 60,000, in particular from 10,00 to 50,000. Preferably, such polymer is used in an amount ranging from 0.05 to 5%, preferably 0.2-1.7% by weight, based on the weight of the detergent.

The following Examples serve to illustrate the invention; parts and percentages are by weight, unless otherwise stated.

Example 1

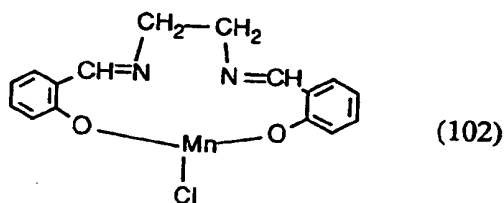
60g of ethylenediamine are dropped into a solution of 277g of salicylaldehyde in 500ml of ethanol over 1 hour at 60°C. Stirring is continued at 60°C. for a further 2 hours and the precipitate so formed is filtered off. There are obtained 260g of a yellow compound having the formula:



corresponding to a yield of 97% of theory.

To 13.4g of the compound of formula (101) dissolved in 1000ml of ethanol there are added 12.25g of manganese(II)-acetate.4H₂O. The dark brown solution so produced is stirred at 75°C. for 3 hours and then evaporated to dryness. The residue is dissolved in 1250 ml of water, filtered and the filtrate is treated with 58g of

NaCl. The precipitated dark brown product is filtered off and dried in vacuum. There are obtained 12.6g of the compound having the formula:



corresponding to a yield of 64% of theory.

Elemental analysis of the compound having the formula (102) and having the empirical formula $C_{16}H_{14}ClMnN_2O_2 \cdot 1.92H_2O$ gives:

15

Req. %	C 49.11;	H 4.60;	N 7.16;	Cl 9.06;	H ₂ O 8.84;	Mn 14.0.
Found %	C 49.4;	H 4.6;	N 7.1;	Cl 8.9;	H ₂ O 8.82;	Mn 13.9.

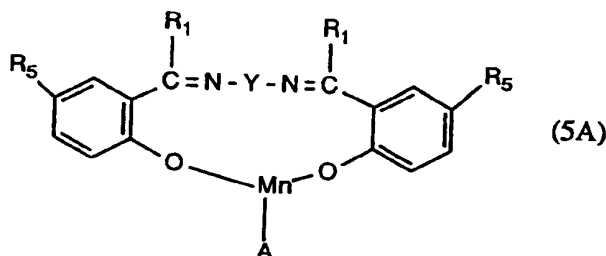
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Example 2

The procedure described in Example 1 is repeated except that 14.1g of manganese-(III)-acetate.2H₂O are used instead of 12.25g of manganese-(II)-acetate.4H₂O. After working up, there are obtained 16g of the compound of formula (102) corresponding to a yield of 81.6% of theory.

Examples 3 to 12

Using the procedure described in Example 1, the following compounds of formula (5A) are prepared:



Example 3 (compound 103):

R₁ is H; R₅ is H; Y is -CH₂CH₂-; and A is CH₃COO.

Elemental analysis of the compound having the formula (103) and having the empirical formula $C_{18}H_{17}MnN_2O_4$ gives:

50

Req. %	C 56.8;	H 4.5;	N 7.4;	Mn 14.5.
Found %	C 56.7;	H 4.6;	N 7.3;	Mn 14.6.

Example 4 (compound 104):

R₁ is H; R₅ is H; Y is -CH₂CH₂-; and A is PF₆.

Elemental analysis of the compound having the formula (104) and having the empirical formula $C_{16}H_{14}F_6MnN_2O_2P \cdot 2.12H_2O$ gives:

EP 0 630 964 A2

R q. %	C 38.1;	H 3.6;	N 5.6;	H ₂ O 7.6;	Mn 10.9.
Found %	C 38.5;	H 3.5;	N 5.7;	H ₂ O 7.6;	Mn 11.0.

5

Example 5 (compound 105):

R₁ is H; R₅ is H; Y is 1,2-cyclohexylene; and A is CH₃COO.

10 Elemental analysis of the compound having the formula (105) and having the empirical formula C₂₂H₂₃MnN₂O₄·1.9H₂O gives:

Req. %	C 56.4;	H 5.8;	N 6.0;	H ₂ O 7.3;	Mn 11.7.
Found %	C 56.2;	H 5.8;	N 5.9;	H ₂ O 7.3;	Mn 11.5.

15

Example 6 (compound 106):

R₁ is CH₃; R₅ is H; Y is -CH₂CH₂-; and A is Cl.

20 Elemental analysis of the compound having the formula (106) and having the empirical formula C₁₈H₁₈ClMnN₂O₄ gives:

Req. %	C 56.2;	H 4.7;	N 7.3;	Mn 17.3.
Found %	C 56.3;	H 4.6;	N 7.1;	Mn 17.1.

25

Example 7 (compound 107):

R₁ is CH₃; R₅ is CH₃; Y is -CH₂CH₂-; and A is Cl.

30 Elemental analysis of the compound having the formula (107) and having the empirical formula C₂₀H₂₂ClMnN₂O₂·4.25 H₂O·0.33 NaCl gives:

Req. %	C 49.1;	H 5.8;	N 5.72;	Cl 9.65;	Mn 11.23.
Found %	C 49.1;	H 5.9;	N 5.6;	Cl 9.8;	Mn 10.8.

35

Example 8 (compound 108):

40 R₁ is H; R₅ is SO₃Na; Y is -CH₂CH₂-; and A is Cl.

Elemental analysis of the compound having the formula (108) and having the empirical formula C₁₆H₁₂ClMnN₂Na₂O₈S₂·3H₂O·1.2NaCl gives:

Req. %	C 28.0;	H 2.6;	N 4.1;	Mn 8.0;	S 9.3.
Found %	C 28.0;	H 2.6;	N 4.1;	Mn 7.8;	S 9.1.

45

Example 9 (compound 109):

50

R₁ is H; R₅ is SO₃Na; Y is -CH₂CH₂-; and A is OH.

Elemental analysis of the compound having the formula (109) and having the empirical formula C₁₆H₁₃MnN₂Na₂O₉S₂·2.0H₂O gives:

Req. %	C 34.2;	H 3.03;	N 5.0;	Mn 9.8.
Found %	C 34.2;	H 3.3;	N 5.6;	Mn 9.3.

55

Example 10 (compound 110):

R_1 is H; R_5 is SO_3Na ; Y is $-\text{CH}_2\text{CH}_2-$; and A is OCH_3 .

Elemental analysis of the compound having the formula (110) and having the empirical formula $\text{C}_{17}\text{H}_{15}\text{MnN}_2\text{Na}_2\text{O}_9\text{S}_2$ gives:

Req. %	C 34.0;	H 2.7;	N 5.0;	Mn 9.9;	S 11.5.
Found %	C 34.8;	H 3.3;	N 5.0;	Mn 10.1;	S 11.2.

Example 11 (compound 111):

R_1 is H; R_5 is SO_3Na ; Y is 1,2-cyclohexylene; and A is CH_3COO .

Elemental analysis of the compound having the formula (111) and having the empirical formula $\text{C}_{22}\text{H}_{21}\text{MnN}_2\text{Na}_2\text{O}_{10}\text{S}_2 \cdot 1.56\text{H}_2\text{O}$ gives:

Req. %	C 39.6;	H 3.6;	N 4.2;	Mn 8.2;	S 9.6.
Found %	C 39.6;	H 4.2;	N 4.9;	Mn 8.7;	S 9.6.

Example 12 (compound 112):

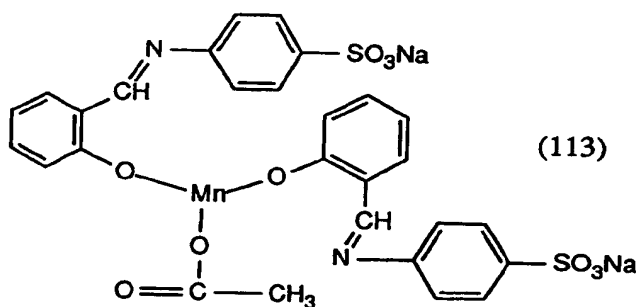
R_1 is H; R_5 is SO_3Na ; Y is 1,2-cyclohexylene; and A is Cl.

Elemental analysis of the compound having the formula (112) and having the empirical formula $\text{C}_{20}\text{H}_{18}\text{ClMnN}_2\text{Na}_2\text{O}_8\text{S}_2 \cdot 2.5\text{H}_2\text{O} \cdot 1.45\text{NaCl}$ gives:

Req. %	C 32.2;	H 3.1;	N 3.8;	Mn 7.4.
Found %	C 32.2;	H 3.1;	N 3.8;	Mn 7.2.

Example 13

Using the procedure described in Example 1, the following compound of formula (113) is prepared:

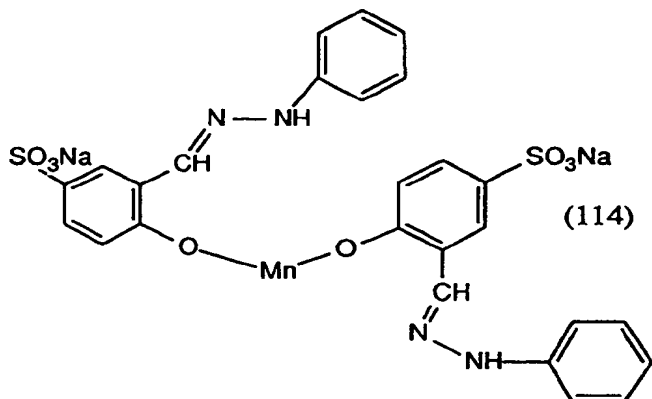


Elemental analysis of the compound having the formula (113) and having the empirical formula $\text{C}_{28}\text{H}_{21}\text{MnN}_2\text{Na}_2\text{O}_{10}\text{S}_2 \cdot 2.5\text{H}_2\text{O}$ gives:

Req. %	C 44.6;	H 3.4;	N 3.7;	Mn 7.3;	S 8.5.
Found %	C 44.6;	H 4.3;	N 3.8;	Mn 7.9;	S 8.7.

Example 14

Using the procedure described in Example 1, the following compound of formula (114) is prepared:

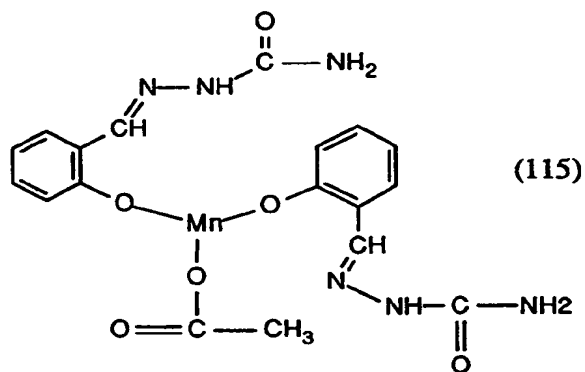


Elemental analysis of the compound having the formula (114) and having the empirical formula $C_{26}H_{20}MnN_4Na_2O_8S_2 \cdot 3.45H_2O$ gives:

Req. %	C 42.0;	H 3.65;	N 7.5;	Mn 7.4;	S 8.6.
Found %	C 42.0;	H 4.6;	N 7.4;	Mn 7.4;	S 8.6.

Example 15

Using the procedure described in Example 1, the following compound of formula (115) is prepared:



Elemental analysis of the compound having the formula (115) and having the empirical formula $C_{18}H_{19}MnN_6O_6 \cdot 2.2H_2O$ gives:

Req. %	C 46.7;	H 3.9;	N 20.7;	Mn 13.3.
Found %	C 45.9;	H 4.1;	N 19.5;	Mn 13.3.

Example 16

Using the procedure described in Example 1, the following compound of formula (116) is prepared:



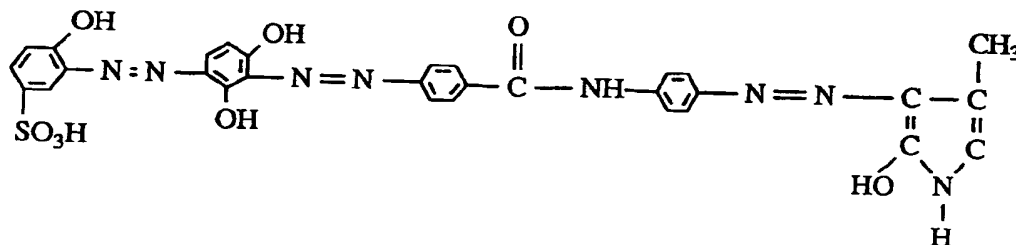
10 Elemental analysis of the compound having the formula (116) and having the empirical formula $C_7H_5MnNNaO_6S \cdot 2.5H_2O$ gives:

Req. %	C 23.7;	H 2.8;	N 4.0;	Mn 15.7;	S 9.1.
Found %	C 23.7;	H 3.2;	N 3.8;	Mn 14.9.	

15 Examples 17 and 18

20 The re-uptake of dyes, which have become detached from a coloured article during the washing process and re-absorbed on to goods which are also being washed and which are thereby discoloured, is evaluated using a test dye, as follows:

The following commercial brown dyestuff is tested at a concentration of 10 mg per litre of wash liquor:



There is then added to this wash liquor, with stirring, in a concentration of 7.5 g. per litre of tap water, a detergent having the following composition:

- 35 6 % Sodium alkylbenzenesulfonate (@Marlon A375);
 5 % Ethoxylated C_{14} - C_{15} fatty alcohol (7 moles EO);
 3 % Sodium soap;
 30 % Zeolite A;
 7.5 % Sodium carbonate;
 40 5 % Sodium metasilicate ($5H_2O$);
 43.5 % Sodium sulphate.

45 The bath is then tested in a "Linitest" beaker for 20 minutes at 30°, 40°, 50° or 60°C., respectively. After the addition, with stirring, directly before the treatment, of x% (see Table 1 below) of sodium perborate monohydrate, and/or of y% (see Table 1 below) of the following compound of formula (117), each based on the weight of the above detergent, the appearance of the bath is evaluated visually:

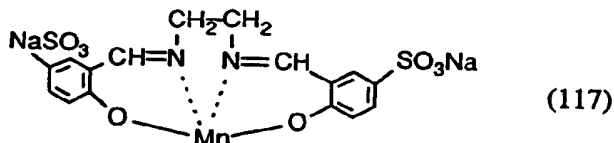


Table 1

Example	Perborate	Compound (117)	Bath Appearance
	x%	y%	
Control	0	0	dark brown
Control	2	0	dark brown
Control	14	0	dark brown
Control	0	0.2	dark brown
Control	0	0.5	slight fade
17	2	0.2	high fade
18	2	0.5	very high fade

The ratings are the same after the treatments at each of the four tested temperatures. They show that the combination of perborate and compound (117) causes a significant decomposition of the test dyestuff in the bath. Accordingly, in corresponding washing baths, very little undesired colouration can occur of textiles which are present in the bath, especially with the lower dye bath concentrations used in practice.

As is evident from Table 1, this effect cannot be obtained in the absence of compound (117) using concentrations of perborate, e.g., 14% by weight, conventionally used in detergents.

Similar results are obtained when the compound of formula (117) is replaced by a compound having one of the formulae (102) to (116).

Examples 19 and 20

The procedure described in Examples 17 and 18 is repeated except that bleached cotton fabric, in an amount of 50g. per litre of wash bath, is also added.

After the wash treatment, over 20 minutes at 30°C., the fabric pieces are rinsed, dried and quickly ironed and their brightness Y is determined using an ICS SF 500 Spectrophotometer.

The difference between the fabric washed without the addition of a dye, and the fabric washed with the addition of the brown dye used in Examples 17 and 18, viz. "ΔY without bleach system" serves as a control rating for the discolouration.

The effectivity of a bleaching system is determined from the equation:

$$\text{Effectivity in \%} = \frac{\Delta Y \text{ without bleach} - \Delta Y \text{ with bleach}}{\Delta Y \text{ without bleach}} \times 100$$

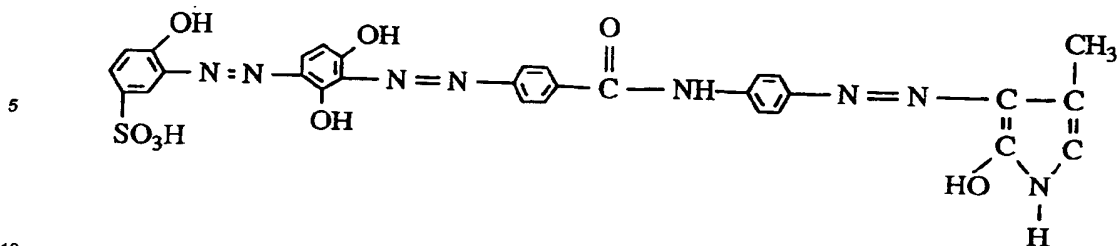
The results obtained are set out in Table 2:

Table 2

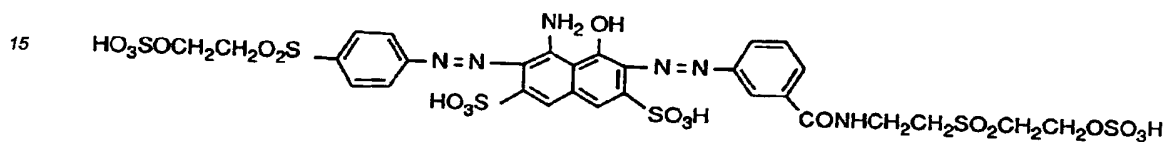
Example	Perborate	Compound (117)	Effectivity
	x%	y%	
Control	0	0	0%
Control	2	0	8%
19	2	0.2	71%
20	2	0.5	76%

Similar results are obtained when the compound of formula (117) is replaced by a compound having one of the formulae (102) to (116).

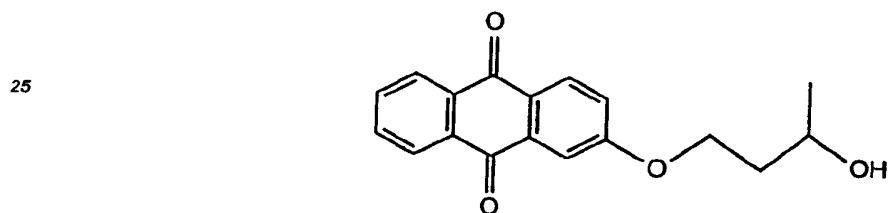
Likewise, similar results are obtained when Example 19 is repeated except that the brown dyestuff of formula:



is replaced by one of the following dyestuffs:



or



Examples 21 and 22

The procedure described in Examples 19 and 20 is repeated except that percarbonate is used instead of perborate.

The results obtained are set out in the following Table 3:

Table 3

Example	Percarbonate	Compound (117)	Effectivity
	x%	y%	
Control	0	0	0%
Control	2	0	31%
21	2	0.2	61%
22	2	0.5	72%

Similar results are obtained when the compound of formula (117) is replaced by a compound having one of the formulae (102) to (116).

Example 23

The procedure described in Examples 19 and 20 is repeated except that there is also added to the bath 2% (see Table 4) of polyvinyl pyrrolidone (PVP), as ®Sokalan HP53, having an average molecular weight of about 40,000, based on the weight of the detergent.

The results are set out in the following Table 4:

Table 4

Example	Perborate	Compound (117)	PVP	Effectivity
	x%	y%	z%	
Control	0	0	0	0%
Control	2	0	0	8%
23	2	0.2	0.5	78%

Similar results are obtained when the compound of formula (117) is replaced by a compound having one of the formulae (102) to (116).

Example 24

The procedure described in Examples 21 and 22 is repeated except that there is also added to the bath z% (see Table 5) of polyvinyl pyrrolidone (PVP), as ®Sokalan HP53, having an average molecular weight of about 40,000, based on the weight of the detergent.

The results are set out in the following Table 5:

Table 5

Example	Percarbonate	Compound (117)	PVP	Effectivity
	x%	y%	z%	
Control	0	0	0	0%
Control	2	0	0	31%
24	2	0.2	0.5	74%

Similar results are obtained when the compound of formula (117) is replaced by a compound having one of the formulae (102) to (116).

Example 25

25g. of bleached cotton fabric are washed for 15 minutes in 200ml. of a bath containing 1.5g. of a detergent having the following composition (ECE standard washing powder):

8.0% Sodium (C_{11.5})alkylbenzenesulphonate;
 2.9% Tallow-alcohol-tetradecane-ethyleneglycolether (14 moles EO);
 3.5% Sodium soap;
 43.8% Sodium triphosphate;
 7.5% Sodium silicate;
 1.9% Magnesium silicate;
 1.2% Carboxymethylcellulose;
 0.2% EDTA;
 21.2% Sodium sulphate; and
 9.8% Water.

After rinsing and drying, the fabric is ironed and evaluated spectrophotometrically using an ICS SF 500 Spectrophotometer.

Washing trials at 30°, 60° and 90°C. indicated, in each case, that the resulting spectra are identical in the visible range, viz. between 400 and 700nm, irrespective of whether the trials are conducted with the above detergent alone, or with the addition of 0.2% by weight of compound (117).

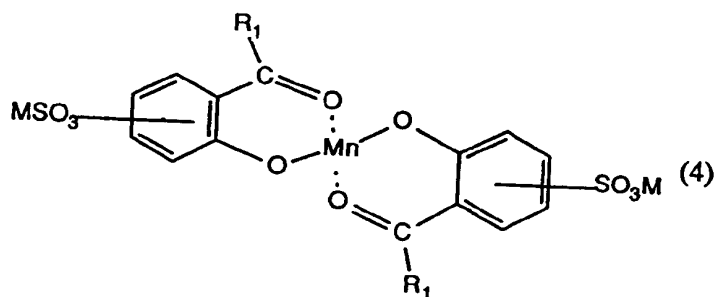
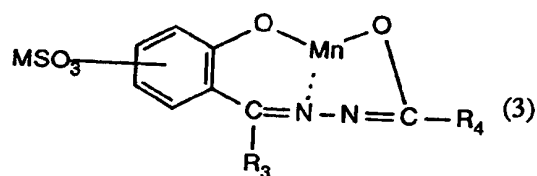
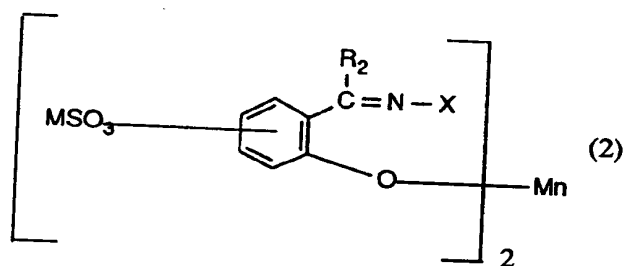
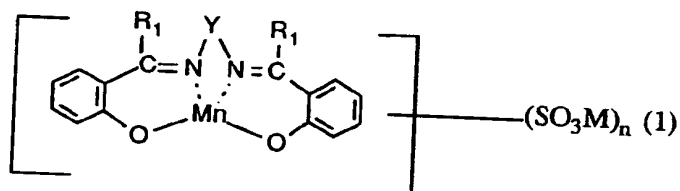
This confirms the visual findings, i.e. that compound does not exhaust on to, and thus cannot impair the appearance of cotton articles.

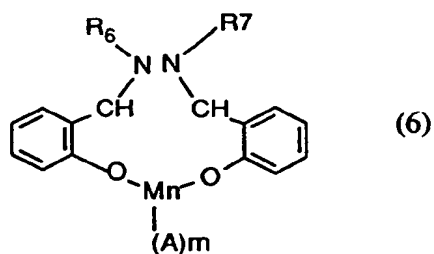
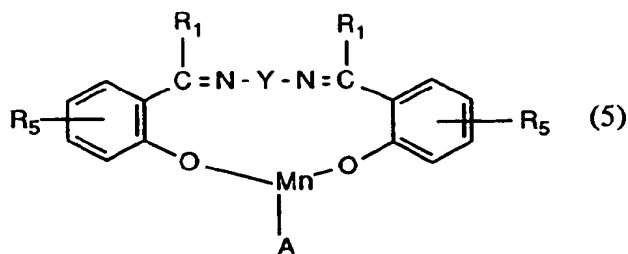
The same trials are repeated but using polyamide (Lilion)-tricot or polyester fabric instead of cotton. Again, with these textile types, there is no undesired discolouration of the washed articles by compound (117) itself.

Similar results are obtained when the compound of formula (117) is replaced by a compound having one of the formulae (102) to (116).

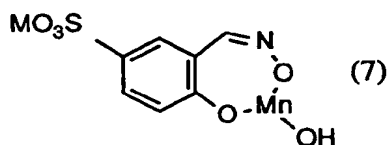
Claims

1. A process for inhibiting the re-absorption of migrating dyes in the wash liquor, comprising introducing into a wash liquor containing a peroxide-containing detergent, from 0.5 to 150 mg. per litre of wash liquor, of one or more compounds having the formula (1), (2), (3), (4), (5), (6) or (7):

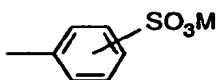




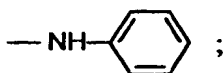
or



in which R_1 , R_2 , R_3 and R_4 are the same or different and each is hydrogen or optionally substituted alkyl, cycloalkyl or aryl; R_5 is hydrogen, alkyl or SO_3M ; R_6 and R_7 are the same or different and each is NH-CO-NH_2 , a group of formula



or a group of formula



Y is optionally substituted alkylene or cyclohexylene; X is OH , NH_2 , optionally substituted aryl or optionally substituted alkyl; n is 0, 1, 2 or 3; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine; m is 0 or 1; and A is an anion.

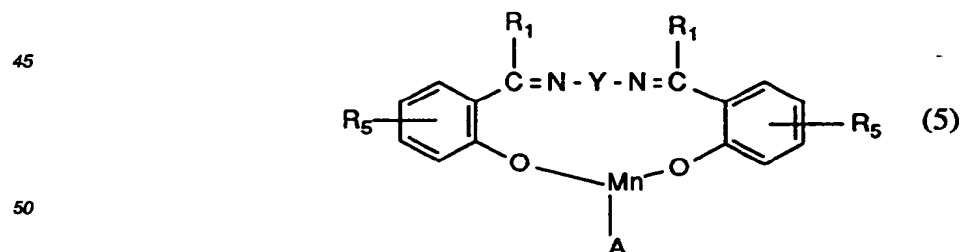
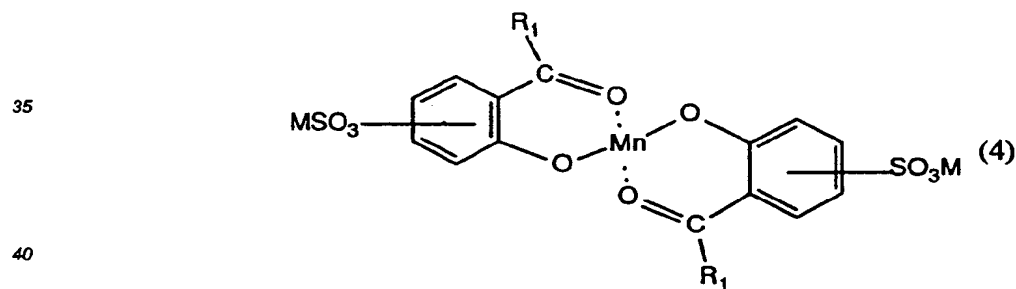
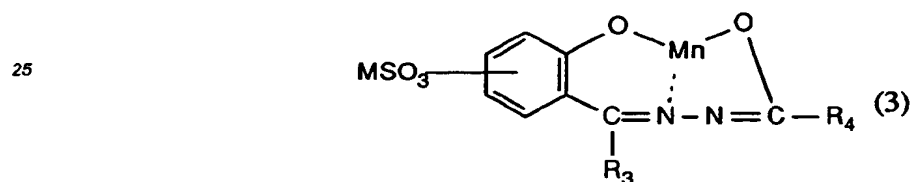
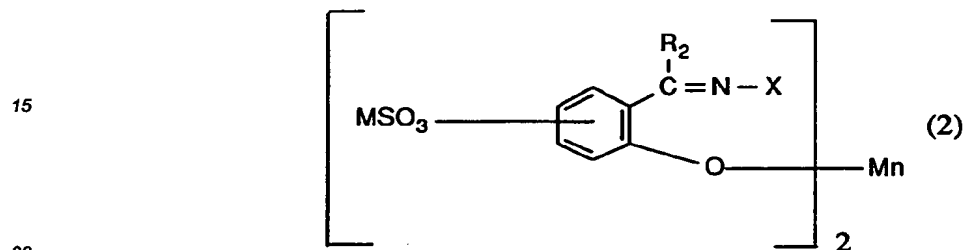
2. A process according to claim 1 in which from 1.5 to 75 mg. per litre of wash liquor of one or more compounds having the formula (1), (2), (3), (4), (5), (6) or (7) is introduced into the wash liquor.
3. A process according to claim 2 in which from 7.5 to 40 mg. per litre of wash liquor of one or more compounds having the formula (1), (2), (3), (4), (5), (6) or (7) is introduced into the wash liquor.
4. A process according to any of claims 1 to 3 in which a compound of formula (1) is used in which R_1 is hydrogen, Y is $-\text{CH}_2\text{-CH}_2-$, M is sodium and n is 2.

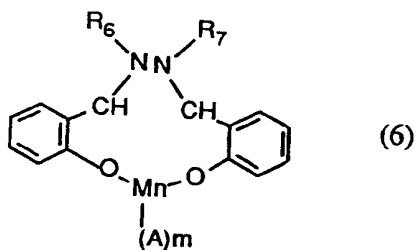
5. A process according to any of claims 1 to 3 in which a compound of formula (2) is used in which R_2 is hydrogen and X is OH.
6. A process according to any of claims 1 to 3 in which a compound of formula (3) is used in which R_3 is hydrogen, R_4 is phenyl and the SO_3M group is in para position with respect to the oxygen atom.
7. A process according to any of claims 1 to 3 in which a compound of formula (4) is used in which R_1 is hydrogen and each SO_3M group is in para position with respect to the oxygen atom.
8. A process according to any of claims 1 to 3 in which a compound of formula (5) is used in which R_1 is hydrogen or methyl, R_5 is hydrogen, methyl or SO_3M , Y is $-CH_2CH_2-$ or cyclohexylene and A is a chloride, acetate, hydroxy, methoxy or PF_6 anion.
9. A process according to claim 8 in which R_5 is in para position with respect to the oxygen atom.
10. A process according to any of claims 1 to 3 in which a compound of formula (6) is used in which R_6 and R_7 are the same, m is 1 and A is the acetate anion.
11. A detergent composition comprising:
 - i) 5-90% of A) an anionic surfactant and/or B) a nonionic surfactant;
 - ii) 5-70% of C) a builder;
 - iii) 0.1-30% of D) a peroxide; and
 - iv) 0.005-2% of E) a compound of formula (1), (2), (3), (4), (5), (6) or (7) as defined in claim 1.
12. A composition according to claim 11 comprising:
 - i) 5-70% of A) an anionic surfactant and/or B) a nonionic surfactant;
 - ii) 5-50% of C) a builder;
 - iii) 1-12% of D) a peroxide; and
 - iv) 0.02-1% of E) a compound of formula (1), (2), (3), (4), (5), (6) or (7) as defined in claim 1.
13. A composition according to claim 12 comprising:
 - i) 5-70% of A) an anionic surfactant and/or B) a nonionic surfactant;
 - ii) 5-40% of C) a builder;
 - iii) 1-12% of D) a peroxide; and
 - iv) 0.1-0.5% of E) a compound of formula (1), (2), (3), (4), (5), (6) or (7) as defined in claim 1.
14. A composition according to any of claims 11 to 13 comprising a combination of two or more of the compounds of formula (1), (2), (3), (4), (5), (6) or (7) as defined in claim 1.
15. A composition according to any of claims 11 to 14 comprising 0.5-5% by weight of a polymer useful in preventing the transfer of labile dyes between fabrics during a washing cycle.
16. A composition according to claim 15 comprising 0.2-1.7% of the polymer.
17. A composition according to claim 15 or 16 in which the polymer is a polyvinylpyrrolidone optionally containing an anionic or cationic substituent.
18. A composition according to any of claims 11 to 17 in which the detergent is in powder or granulate form.
19. A composition according to any of claims 11 to 18 in which the detergent is in liquid form and contains 0-5% water.
20. A composition according to claim 19 in which the detergent is in liquid form and contains 0-1% water.
21. A process for the production of a detergent as claimed in claim 18 in which the components of the detergent are mixed in dry form.
22. A process for the production of a detergent as claimed in claim 18 in which a base powder is produced by spray-drying an aqueous slurry which contains all the components defined in claim 11, apart from the components D) and E); and then adding the components D) and E) by dry-blending them into the base powder.

23. A process for the production of a detergent as claimed in claim 18 in which the component E) is added to the slurry containing components A), B) and C), which slurry is then spray-dried before component D) is dry-blended into the mixture.

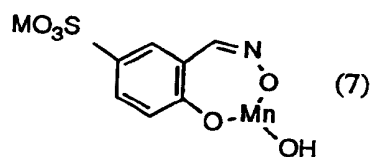
24. A process for the production of a detergent as claimed in claim 18 in which component B) is not present, or is only partly present in a slurry containing components A) and C); the component E) is incorporated into component B), which is then added to the spray-dried base powder; and finally component D) is dry-blended into the mixture.

25. A compound having the formula (2), (3), (4), (5), (6) or (7):

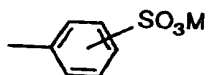




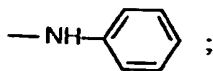
10 or



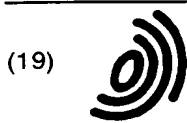
25 in which R₁, R₂, R₃ and R₄ are the same or different and each is hydrogen or optionally substituted alkyl, cycloalkyl or aryl; R₅ is hydrogen, alkyl or SO₃M; R₆ and R₇ are the same or different and each is NH-CO-NH₂, a group of formula



or a group of formula



40 Y is optionally substituted alkylene or cyclohexylene; X is OH, NH₂, optionally substituted aryl or optionally substituted alkyl; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine; m is 0 or 1; and A is an anion.



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(11) **EP 0 630 964 A3**

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:
09.10.1996 Bulletin 1996/41

(43) Date of publication A2:
28.12.1994 Bulletin 1994/52

(21) Application number: **94810345.2**

(22) Date of filing: **10.06.1994**

(51) Int Cl.⁶: **C11D 3/34, C11D 3/26,
C11D 3/32, C11D 3/39,
C07F 13/00, C07C 251/24,
C07C 281/14, C07C 309/49**

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI NL PT SE

(30) Priority: **19.06.1993 GB 9312693
08.12.1993 GB 9325117**

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(54) **Inhibition of re-absorption of migrating dyes in the wash liquor**

(57) A process for inhibiting the re-absorption of migrating dyes in the wash liquor comprises introducing into a wash liquor containing a peroxide-containing detergent, from 0.5 to 150 mg, per litre of wash liquor, of

one or more manganese complexes. The manganese compounds do not exhaust at all on to cotton, polyamide or polyester fibres so that the compounds cannot lead to fibre discolouration problems.

EP 0 630 964 A3

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 81 0345

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	WO-A-91 14694 (RES CORP TECHNOLOGIES) 3 October 1991 * claims; figures 2,8; examples *	25	C11D3/34 C11D3/26 C11D3/32 C11D3/39 C07F13/00 C07C251/24 C07C281/14 C07C309/49
X	WO-A-93 03838 (RES CORP TECHNOLOGIES INC) 4 March 1993 * page 68; table VII *	25	
X	US-A-3 173 956 (R.GRINSTEAD) 16 March 1965 * claims; examples *	25	
D,X	US-A-4 655 785 (REINERT GERHARD ET AL) 7 April 1987 * claims *	25	
A	EP-A-0 538 228 (PROCTER & GAMBLE) 21 April 1993 * claims; examples *	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C11D C07F C07C
Place of search THE HAGUE		Date of completion of the search 6 August 1996	Examiner Pfannenstien, H
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